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FIRST QUARTERLY PROGRESS REPORT ON

THE EVALUATION OF HIGH TEMPERATURE MATERIALS

For:

Mr. Lawrence N. Hjelm
Research and Technology Division
Wright-Patterson Air Force Base, Ohio

Contract No. AF 33(615)-1312

Date:

10 April 1964

Period Covered:

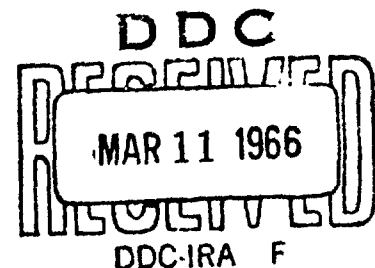1 January 1964 through 31 March 1964

Submitted by:

University of Dayton
Research Institute
Dayton 9, Ohio

Prepared by:

John C. Wurst
John A. Cherry
Norman L. Hecht

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ABSTRACT

Work under the subject contract is divided into two general areas: one covering the evaluation of refractory alloy coatings; the other the evaluation of high temperature materials systems.

The coatings evaluation program is directed towards the development of an orderly series of standardized test procedures to provide a common basis for comparison of the characteristics of various refractory alloy coating systems and their applicability to certain service requirements. The program is intended to evaluate (1) the ability of the coatings to provide reliable oxidation protection; and (2) the extent to which the coating and/or application process may influence the properties of the substrate material.

The evaluation of high temperature materials is intended to provide data pertaining to the performance of materials in unusual thermal and corrosive environments. While the bulk of this effort is centered about arc-plasma-jet testing, investigations in related areas, including microstructural analysis, experimental fabrication, mechanical properties, and oxidation behavior, may be pursued in the course of an evaluation.

EVALUATION OF REFRACTORY ALLOY COATINGS

INTRODUCTION

The University of Dayton is currently engaged in a program to evaluate coated refractory alloy sheet for structural applications. The objectives of this effort are to develop data relating to (1) the oxidation resistance of coatings; (2) the effects of coatings and/or coating processes upon the mechanical and physical properties of substrate alloys; and (3) the loadbearing capability of coated alloys at elevated temperatures.

The program, which is a continuation of an earlier effort under Contract AF 33(616)-7838, is not oriented towards any particular end use, but is intended to provide basic coating performance information to aid in the intelligent selection of coating systems for prospective applications.

The present evaluation includes:

metallographic analysis;
bend transition temperature measurements;
tensile strength measurements;
cyclic oxidation tests in the range of 1600° to 3000°F with a failure rate analysis at 2600°F;
stress-rupture tests in a full factorial experiment.

Metallographic analysis includes visual examination of the substrate microstructure and microhardness measurements primarily to evaluate the quality of the coating and to determine if any detrimental side effects resulted from the coating process.

The bend transition temperature and tensile tests relate the effects of the coating and its application process to the mechanical properties at and near room temperature. The bend test evaluates ductility and changes in transition temperature resulting from base metal contamination and/or recrystallization. The tensile tests also provide information regarding ductility, but are performed primarily to measure any loss of tensile strength.

Bend transition temperature is defined as the lowest temperature at which a 90° free bend can be formed about a radius four times the thickness (T) of a rectangular 1-1/4" x 1/2" test tab. The procedures of this test and the bend fixture employed are in accordance with recommendations of the Materials Advisory Board (MAB Report 189M). The only deviation from these specifications is the time of bend which was increased from 400T seconds to 200T minutes to enable the test operator to visually and audibly detect a brittle specimen failure.

ASTM specifications for sheet metal testing serve as a general guide for tensile tests. These tests are performed at a strain rate of 0.05 in/in/min, normally at room temperature.

Cyclic oxidation tests are conducted on 1-1/4" x 1/2" coated tabs at temperatures of 1600°, 2400°, 2600°, and 3000°F. Specimens are cycled to room temperature at one-hour intervals for weighing and inspection and are considered failed when weight change and visual inspection reveal evidence of gross substrate oxidation. At 2600°F sufficient tests are performed to fit the resultant data to the Weibull failure probability function. Graphical techniques are then employed to estimate coating capability and reliability.

The stress-rupture testing is essentially an evaluation of the structural capabilities of a coated alloy when subjected to exposures of several hours duration in an oxidizing environment at specific levels of stress and temperature. These tests are performed with conventional lever arm creep frames, using 1-1/2" x 6" test specimens radiantly heated along a 1-3/4" gage length by an inductively coupled susceptor furnace. The apparatus includes recording differential transformers for the continuous measurement of specimen elongation during test.

Rather than develop stress-rupture and creep behavior from a series of individual tests at different stress levels and temperatures, a statistically-designed experiment is employed. This consists of a replicated full factorial experiment (with all factors assumed fixed) containing three levels of stress, three levels of temperature, the testing machine identity, and two coating batches.* This technique was chosen because, in addition to providing sufficient data for a conventional presentation of creep and stress-rupture properties, it offers an opportunity through proper statistical analysis to estimate the relative effect of each input and/or interaction of inputs upon these properties. It also affords an opportunity to evaluate the influence of uncontrolled factors such as specimen variability and variations of the test environment.

Current refractory alloys of interest include TZM molybdenum and the columbium alloys, D43 and C129Y. It is anticipated that additional refractory alloys will be added as the program progresses.

To allow a maximum number of coating-alloy combinations to be represented in the program, the evaluation procedure is split into two phases. The first is essentially a screening phase consisting of complete metallographic analysis of the "as coated" alloy, tensile strength and bend transition temperature measurements, and cyclic oxidation tests. Based upon the results of this screening, two coatings per alloy are selected for Phase II testing which includes the full factorial stress-rupture test and a replication of the screening tests with a second set of specimens to characterize batch-to-batch variability of the coating system.

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*Vendors are requested to coat the stress-rupture specimens in two groups, either in two separate retorts or in two separate operations of the same retort, so that batch-to-batch variability of the coating process can be evaluated.

CURRENT STATUS

The current program will include a re-evaluation of coated TZM using sheet metal produced by Universal Cyclops Corporation under a BuWeps contract. This will be a cooperative effort of BuWeps and RTD with Southern Research Institute and the University of Dayton as principle contractors.

Prior to actual fabrication and coating of test specimens, the machining and finishing procedures of both contractors are being evaluated. Trial specimens have been prepared by SRI and UD and will be shipped to Pfaudler and Chromalloy for coating upon completion of the pre-coating inspection. The two coating vendors have been requested to perform their own inspection of these specimens prior to coating application.

If no problems arise from substrate delamination and current fabrication techniques are judged suitable for this program, preparation of test specimens will be initiated upon completion of this study.

Phase I evaluation of coated D43 columbium has proceeded sufficiently to select two coatings for Phase II evaluation. Metallographic analysis, bend transition temperature measurements (for five of the six systems), tensile testing, and cyclic oxidation at $2600^\circ F$ have been completed. Cyclic oxidation tests at 1600°, 2400°, and $3000^\circ F$ are now in progress.

Tensile tests have been completed for the C129Y coated specimens, as have cyclic oxidation tests at $2600^\circ F$ and bend transition temperature measurements. Metallographic analysis is currently in progress and will be discussed in a subsequent quarterly report.

SPECIMEN PROCUREMENT

Both the D43 (Cb-10W-1Zr) and C129Y (Cb-10W-10Hf) columbium alloys were procured as 20 mil sheet. The D43 was obtained from E. I. duPont; the C129Y, from Wah Chang Corporation.

These alloys were coated by the same six vendors: Thompson Ramo Wooldridge (TRW), Chromizing Corporation, General Telephone & Electronics Laboratories (GT&E), Pfaudler, LTV Corporation, and the Boeing Company.

Each vendor applied the same coating to each alloy. Their designations for each of these coatings are as follows:

Vendor	Coating Designation
TRW	Cr-Ti-Si
Chromizing	Durak KA
Pfaudler	PFR-32 (Modified Single Cycle Silicide)

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Vendor	Coating Designation
GT&E	R508 (Ag-Si-Al Slurry Silicide)
LTV	Cr-B (Modified Two-Cycle Silicide)
Boeing	Disil (Fluidized Bed Silicide)

GT&E reported some difficulties with "blobbing" of the C129Y coating during a diffusion treatment and coating thickness of these specimens was quite non-uniform. No difficulties of this nature were experienced with the D43 specimens. The D43 specimens were coated by GT&E in two batches: the bend and oxidation tabs in one batch; the tensile specimens in another. The average weight gain of the tensile specimens were 20% less than the other specimens, an indication that these specimens received a thinner coating. No reason was stated for coating these specimens in two batches. Presumably the C129Y specimens were coated in one batch since multiple batching was not mentioned in the cover letter which accompanied the coated specimens.

Boeing had difficulty in Disil coating the D43 specimens and found it necessary to pickle the specimens to achieve a proper surface finish. The pickling treatment removed approximately 1.0 mil of material from each side of the specimens. Despite this surface treatment, Boeing did not anticipate good performance of their coating on this alloy. In contrast, the C129Y specimens were Disil coated without difficulty.

METALLOGRAPHIC ANALYSIS

Photomicrographs of the D43 specimens are shown in Figures 1, 2, and 3, and the pertinent metallographic data are presented in Table 1.

In general, substrate coverage appeared to be good and all of the coatings were fairly uniform in thickness, except for the GT&E system which varied from 7.2 to 13.6 mils. This was the thickest of the six coatings. The others ranged from an average of 1.2 mils (Chromizing) to 3.6 mils (LTV). The Pfaudler, Chromizing, LTV, and Boeing coatings all were thicker at the edge, which previous experience has shown to be characteristic of silicide coatings.

The Pfaudler, Chromizing, and Boeing coatings showed no evidence from visual examination or microhardness measurements of any diffusional reactions between coating and substrate. The LTV, TRW, and GT&E systems exhibited three, two, and two diffusional layers, respectively. Furthermore, the outer diffusion zone of the TRW coating contained many "islands" which were harder than the surrounding matrix. Similar hard islands were observed in the coating proper of the GT&E system.

The metallographic specimens were not etched because of possible damage to the coatings and other zones adjacent to the substrate. Therefore, substrate microstructure could not be visually examined; however, the lack of appreciable hardness change after coating would suggest that none of the coating processes produced significant changes in microstructure of the base metal.

Each coating process produces some reduction of substrate thickness. This ranged from 0.6 mils/side for the PFR-32 coating to a maximum of 1.9 mils/side for the LTV two-cycle silicide.

BEND TRANSITION TEMPERATURE

Bend transition temperature data for the D43 and C129Y specimens are summarized in Tables 2 and 3. Lowest test temperature was -50°F, which was above the transition temperature of both uncoated alloys.

D43 Columbium Alloy

Of the D43 systems tested, the TRW, Chromizing, Boeing, and GT&E coatings maintained a bend transition temperature below -50°F, while the bend transition temperature of the LTV specimens increased to between 0° and 25°F and that of the Pfaudler samples increased to between 75° and 125°F.

C129Y Columbium Alloy

Only the LTV and Pfaudler C129Y coatings showed an increase in bend transition temperature. The other four coatings maintained bend transition temperatures below -50°F. The LTV system exhibited an increase to between 0° and 25°F, and the Pfaudler system increased to between 125° and 150°F.

TENSILE TESTING

Tensile tests were conducted at room temperature, in most instances, in triplicate. Test results for both D43 and C129Y coatings are summarized in Tables 4 and 5 and Figures 4 through 7.

D43 Columbium Alloy

In the D43 tests, the LTV specimens were least affected, with virtually no loss in ultimate strength and a slight gain (9%) in yield strength. The Boeing coating system, with approximately 40% loss of yield and ultimate strength, and the TRW specimens, with corresponding losses of 24% and 27%, were the most severely degraded.

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All of the D43 specimens experienced some loss of room temperature ductility as was evidenced by a decrease of ultimate elongation. It is interesting to note that, of the two coatings which displayed the greatest loss of strength, the Boeing coating produced the least reduction of ultimate elongation (22%), whereas the TRW specimens exhibited the greatest at 53%.

C129Y Columbium Alloy

The retained tensile properties of the C129Y specimens after coating were better than the D43 specimens. The Chromizing specimens, with an increase of 1% in yield strength and a reduction of only 4% in ultimate strength, were the least affected. whereas the TRW and Boeing samples, both of which experienced a 23% loss of yield and ultimate strengths, were the most severely affected.

All but the Pfaudler specimens showed an average increase in ultimate elongation, rather than a decrease as would be expected. It is possible that the sheet was not annealed prior to coating and that the various coating processes completely or partially annealed the alloy, thereby increasing its ductility. If true, this will be verified by the metallographic analysis presently being conducted.

CYCLIC OXIDATION TESTS

Cyclic oxidation data for the D43 and C129Y tests at $2600^{\circ}F$ are presented in Tables 6, 7, 8, and 9 and in the form of Weibull plots in Figures 8 through 17.

D43 Columbium Alloy

The Chromizing, Pfaudler, and Boeing coated D43 specimens all exhibited relatively poor oxidation resistance. The ten Chromizing specimens failed in less than six hours and because of the limited number of data points, it was impossible to generate a Weibull representation of the failure distribution. The Pfaudler specimens formed a Weibull failure distribution slope of 1.7 and a maximum probable life of ten hours. The Boeing samples exhibited a 3.1 Weibull slope (close to a normal distribution) and a maximum probable life of fourteen hours. The LTV specimens failed along a Weibull slope of 2.4 with a maximum probable life of 44 hours. The failure distribution for the TRW coating group followed a Weibull slope of 1.3 with a maximum expected life of 90 hours.

The GT&E demonstrated the best cyclic oxidation resistance of the six systems tested. This was not unexpected in view of the relative thickness of the coating. In this group of ten specimens, the first failures occurred at

63 hours, which exceeded the longest time to failure of any other coated D43 specimen. The Weibull slope for the GT&E group was 4.3 with a maximum probable life of 180 hours.

Estimates of reliability at 70%, 90%, and 95% probabilities of survival were determined from the Weibull plots. The GT&E coating was clearly the most reliable of the group, followed by two systems of nearly equal reliability, the LTV and TRW coatings.

C129Y Columbium Alloy

The C129Y cyclic oxidation tests also showed a marked difference among the six coating systems evaluated. The Pfaudler specimens were the poorest, with all the specimens failing at the sixth hour of test. The LTV and Chromizing specimens were only slightly better. The LTV specimens formed a Weibull slope of 0.7 for a maximum expected life of 20 hours, whereas the Chromizing samples followed a slope of 2.0 with a maximum probable life of 13 hours.

The Boeing group exhibited the only bimodal failure distribution of these tests. The initial failure followed a 0.7 distribution slope to 17 hours and a slope of 1.7 thereafter. Maximum probable life of this coating was 39 hours.

The TRW and the GT&E coatings demonstrated excellent oxidation resistance as compared to the others. The TRW specimens formed a distribution slope of 2.7 with a maximum expected life of 95 hours. The GT&E specimens followed a relatively steep Weibull slope of 12.6 to a maximum probable life of 160 hours. The time to failure of the first GT&E specimen was 68 hours, which exceeded the maximum expected life of all the others except the TRW coating. These two coatings also ranked first and second in estimated reliability. At the 95% level, estimates of life time were 95 hours for the GT&E coating; 20 hours for the TRW coating.

DISCUSSION

The two D43 coatings selected for Phase II evaluation were the GT&E and TRW systems. These were chosen because of their performance in cyclic oxidation, their retention of a low bend transition temperature, and their tensile properties after coating.

Because of the wide variability of coating thickness of the Phase I GT&E specimens and the apparent limited process facilities of this company (as evidenced by the necessity to batch coat the Phase I specimens), batch-to-batch and specimen-to-specimen variability will receive careful attention in the Phase II evaluation of this coating. The uniqueness of this coating and its

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demonstrated capability were considered sufficient to offset the liability of apparent processing difficulties and thereby justify further evaluation of this system.

FUTURE WORK

During the next reporting period, it is anticipated that:

1. Phase II testing of GT&E and TRW coated D43 will be completed;

2. Phase II testing of coated C129Y will be initiated;

3. preparation of specimens for TZM evaluation will be initiated.

HIGH TEMPERATURE MATERIALS EVALUATION

In recent years, the high temperature materials evaluation program at the University of Dayton has expanded from arc-plasma-jet testing of materials into a variety of related areas. In addition to the routine screening of candidate materials according to general procedures outlined by the Refractory Composites Working Group, a number of specialized plasma-jet tests have evolved. These include a test to measure the oxidation resistance and upper useful temperature limits of refractory composites, low heat flux testing for specialized applications, high temperature compatibility studies of materials in various corrosive media, and the thermal shock testing of plasma-sprayed coatings. Other work includes the low pressure oxidation testing of refractories and the optimization of plasma-sprayed, metal-graded ceramics. Areas under active investigation are discussed in subsequent sections of this report.

ARC-PLASMA-JET TESTING

The arc-plasma-jet testing of materials for which no specific application is being considered generally follows the procedures outlined by the Refractory Composites Working Group. In these tests, 2" x 2" x 1/2" specimens are oriented at 45% to the subsonic effluent of the plasma-jet at a position 1-1/8" from the exit plane of the torch. The plasma-jet is stabilized with a simulated air mixture of 80% N_2-20% O_2 and operated at a standard mass flow of 0.0082 lb/sec. Test levels are controlled as a function of heat flux to a 1/2" diameter water-cooled copper calorimeter.

Experimental Methods

Prior to the exposure of a test sample, the properties of the arc effluent are determined from measurements of the following parameters:

1. nitrogen and oxygen flow rate;

2. input power to the arc;

3. power losses to the coolant;

4. heat flux at the sample location;

5. stagnation pressure at the sample location.

From these measured values, the following properties are calculated:

1. effluent velocity at the sample;

2. effluent enthalpy at the nozzle exit;

3. effluent temperature at the nozzle exit.

Following this calibration procedure, samples which had previously been measured and weighed are introduced into the effluent for test. During test, the front and back surface temperatures of the sample are continuously recorded as a function of time. Front surface temperatures are also monitored periodically with the optical pyrometer.

Immediately after test, the calibration procedure is repeated as a recheck of the initial measurements. Samples are photographed after test and the following physical measurements taken: depth and volume of erosion, density, and weight.

Manufacturer I

Twelve specimens of foamed zirconia in three densities (1.0, 1.1, and 1.24 gms/cc) were evaluated at 275 Btu/ft^{2}sec for 300-second exposures according to the general procedures described in the preceding section. Half of the specimens (two of each density) were phenolic resin impregnated by University personnel with approximately 30 to 40 w/o resin. Thus, duplicate tests were performed on each foam density, two unfilled and two with resin impregnant.

The results of these tests are summarized in Tables 10 and 11 and the corresponding temperature-time histories are shown in Figures 18 and 19.

The performance of the unfilled foams was rather impressive. Unlike previously evaluated foamed zirconia from this manufacturer and others, which failed in thermal shock after a few seconds of heating, these specimens all survived a full 300-second exposure. Thermal stress cracking was observed with both of the two low density foams and one each of the medium and high density foams. These failures were evident from the back surface temperature behavior which either stabilized at a higher level or increased abruptly at the time of thermal stress cracking. Front surface temperatures of the unfilled foams were coincident; however, back surface temperatures stabilized at levels inversely proportional to foam density. Despite these failures, attrition of material was only minor and in no instance did weight loss exceed 2%.

The phenolic resin impregnated specimens experienced virtually no erosion, nor was there any evidence of thermal stress cracking. Back surface temperatures during the initial heating period remained at room temperature

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for the first 75 seconds of test. Only after substantial loss of the ablative resin (at approximately 125 seconds) was the influence of foam density upon thermal insulating ability discernible. The low and medium density foams followed nearly the same back surface temperature profile. The high density foam ran somewhat cooler throughout each test.

Final specimen temperatures of the impregnated samples, both front and back surface, followed the same relative order with the low density foam the highest; the high density foam the lowest.

PLASMA COATING STUDIES

An investigation of composite metal-ceramic systems formed by plasma spraying has been initiated. To date, coatings of $NiAl-Al_2O_3$, NiAl-Ni coated $Al_2O_3-Al_2O_3$, and $NiCr-ZrO_2$ systems have been evaluated. These were plasma-sprayed on stainless steel substrates, metallographically studied, and subjected to bond strength tests. These initial studies provided guidance for a more intensive and systematic investigation into the critical aspects of composite coatings.

The materials were sprayed with a Plasmadyne SG-1 plasma torch using argon as the arc gas and nitrogen as the powder carrier gas. The spray powder was fed into the nitrogen gas stream by a screw feed hopper system specially designed by personnel of the Research Institute.

Specimens were prepared with each of the following coatings:

.002"-.003" NiAl and .015" Al_2O_3;

.001"-.002" NiCr and .010" ZrO_2;

.002" NiAl, .006" Ni coated Al_2O_3 and .006" Al_2O_3;

.002" NiAl, .006" graded $_3$ and .006" Al_2O_3;

.002" Mo, .004" graded $NiCr-ZrO_2$ and .005" ZrO_2.

The graded zones of the latter three composites consisted of three layers, each approximately .002" thick, premixed in the following volume ratios: 65% ceramic-35% metal, 85% ceramic-15% metal, and 95% ceramic-5% metal.

The particle size of all powders with the exception of the ceramic powders used in the graded blends were between 250-325 mesh (63-44μ). The ceramic powders used in the graded blend were 170-250 mesh (88-66μ). The particle size was controlled by screening the powders in a Tyler Ro-Tap sieve

shaker. Prior to screening, all the powders were vacuum dried. Desiccation of powders was maintained until spraying. The spray powders used were purchased from the following vendors:

1. ZrO_2 - Zircoa Corporation;

2. Al_2O_3 - Norton Company;

3. Mo and NiAl - Atlantic Equipment Engineers;

4. Ni coated Al_2O_3 - Sherritt Gordon Mines, Ltd.

The spray settings and distances for each material were determined from slide distance tests performed according to the technique developed by Moore (Ref. 1). The spray distance varied from 3" - 5" and the power settings varied from 18-30 KW. The flow rate for the argon arc gas was 128 cfh and for the nitrogen carrier gas was 36 cfh. Specific spray conditions are given for each coating in Table 12.

Six specimens were prepared (five for bond strength testing; the sixth for metallographic analysis) by spraying on stainless steel plates 1" x 1" x 1/8" which had been abraded, cleaned, and desiccated until the coating operation.

For bond strength determinations, the coated specimens were epoxy bonded between two test blocks and then loaded with a universal testing machine in a direction normal to the plane of the coating. The load was slowly increased until coating failure occurred. Bond strength was defined as the breaking load divided by the coating surface area. These specimens were then examined under 100x magnification to determine the mode of failure. The data obtained from these tests are also compiled in Table 12.

In general, the bond strength measurements were quite reproducible and in agreement with reported values (Refs. 2 and 3). Only in a few instances were individual values significantly different from their group averages. Failure location was also fairly consistent within each group.

The lowest bond strengths were measured with the ungraded $NiAl-Al_2O_3$ coating which failed consistently in the NiAl layer at an average bond strength of 485 psi. The ungraded $NiCr-ZrO_2$ system, on the other hand, exhibited a much higher average bond strength (1480 psi) with all failures occurring in the ZrO_2 layer. Bond strengths were significantly improved with the addition of an intermediate graded zone. In this respect, the use of a $NiAl-Al_2O_3$ mixture proved more effective than Ni coated alumina as evidenced by the respective average bond strengths of the two coatings (860 and 1760 psi).

High bond strengths (2690 psi average) were obtained with the NiCr-ZrO_2 graded ZrO_2 coating. Significantly, all failures of the graded coatings occurred either at the graded zone-topcoat interface or in the topcoat. No failures in or near the metal flash coat were observed.

Microscopic analysis revealed that the most uniformly graded intermediate layer was the Ni coated Al_2O_3 system and the most non-uniform, the NiCr-ZrO_2 system which was metal-rich throughout the zone. It is interesting to note that the coating with the most uniformly graded intermediate layer (Ni-Al, Ni coated Al_2O_3-Al_2O_3) had the lowest bond strength and the system with the most non-uniformly graded intermediate layer (Mo, NiCr-ZrO_2, ZrO_2) had the highest bond strength.

The results of this preliminary investigation indicated several areas which will require further study. In particular, the role of the graded zone as it affects bond strength and the influence of grading uniformity and particle size ratio should receive attention. Accordingly, future studies will investigate:

1. the influence of metal and ceramic powder size in various blends of the NiCr-ZrO_2 system plasma-sprayed on Mo primed stainless steel;

2. the bond strength of NiAl, Mo, and NiCr on stainless steel substrates;

3. the relation of bond strength to gradation uniformity and ceramic-to-metal ratio.

INVESTIGATION OF LOW PRESSURE EFFECTS ON THE OXIDATION RESISTANCE OF SELECTED CERAMIC COMPOSITES

The use of protective surface coatings and/or the inclusion of oxidation resistant phases near the surface of structural materials susceptible to oxidation at elevated temperatures has been relatively successful. Silicide compounds in particular have proved useful in providing oxidation protection by either technique.

When exposed to elevated temperatures in an oxygen atmosphere, the silicide forms an impervious glassy silicate. This glassy phase at the surface prevents oxygen penetration and reaction with underlying material. At atmospheric pressure, this protective system works well to temperatures in excess of 3000°F. However, recent investigations of protective coating systems for refractory metals at low pressures (0.5-10 mm Hg) and elevated temperatures (3000°F) have shown that catastrophic failure can occur due to the volatilization of the protective material. While pressure sensitivity has been identified as a problem with thin surface coatings, the effect of reduced vapor pressures on thick composite ceramics has not been extensively explored.

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An investigation has been initiated to determine the effects of low pressure upon the oxidation behavior of several selected ceramic composites. Samples of Boride Z (86 ZrB_2 13 $MoSi_2$, 1 BN), JTA graphite (a composite graphite containing ZrB_2 and Si), a modified silicon carbide (high density SiC with a minor percentage of Si), and normal SiC were exposed for 20 minutes to $3000°F$ in air at pressures of 760, 10, and 0.5 mm Hg. The results of these tests are described in Table 13.

Five samples of each of the materials were tested for twenty minutes at each of the test levels. The low pressure tests (at 0.5 and 10 mm) were conducted in a specially designed, induction-heated alumina tube furnace using high purity Al_2O_3 as the support medium. The atmospheric tests were conducted in a resistance-heated box furnace, also with Al_2O_3 specimen supports.

Each sample was weighed and visually examined before and after exposure. A section was cut from each of the tested samples and studied under 90x magnification with a stereo microscope.

On exposure to low pressure and high temperatures, all of the composite systems showed a weight loss. The effects at 0.5 mm were similar to those observed at 10 mm, but less severe. The limited amount of oxygen at 0.5 mm Hg was not sufficient for complete coating formation or severe oxidation. Boride Z was the least affected and the silicon carbide systems the most affected by the test environment. The protective coatings formed on the surface of the Boride Z and JTA specimens at low pressure were crystalline, while similar specimens tested at atmospheric pressures had glassy surface coatings. This is probably due to the volatilization of B_2O_3 which has a low vapor pressure and is a major glass former in these systems. Also of interest was the presence of a dark intermediate phase observed in the Boride Z specimens tested at 10 and 760 mm Hg (see Figure 20). This darkened zone is probably due to a deficiency of BN and $MoSi_2$ in this region as the result of diffusion to the surface. The coatings which formed on the surface of JTA and the modified SiC at 10 mm Hg were non-adherent and easily parted from the specimens. At 10 mm pressure, continuous coatings were not formed and in the case of the modified SiC, the glassy coating was barely visible.

For purposes of comparison, the test materials were exposed to a $3000°F$ environment at standard pressure. Under these conditions, tightly-adherent glassy films formed on the surface of all the materials. In the case of JTA, the glass coating appeared to be porous which may account for the small weight loss recorded. All the other materials showed a weight gain at 760 mm.

The weight loss observed at low pressure (0.5 and 10 mm Hg) indicated volatilization of test materials had occurred. It also appeared that the protective coatings formed by the JTA and SiC systems upon exposure to low

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pressure/high temperature were not effective. Although the protective coatings formed on the surface of Boride Z specimens were fairly effective under the test environment, it is not known if this effect is continuous to 760 mm Hg.

The Boride Z material has been singled out for further study on the basis of its performance in these tests. An investigation (including x-ray analysis) of the effect of pressure on the coating phases formed and a further study of the intermediate zone formed in the Boride Z material is planned. Hardness analysis of the surface and the interface of the coatings are also planned.

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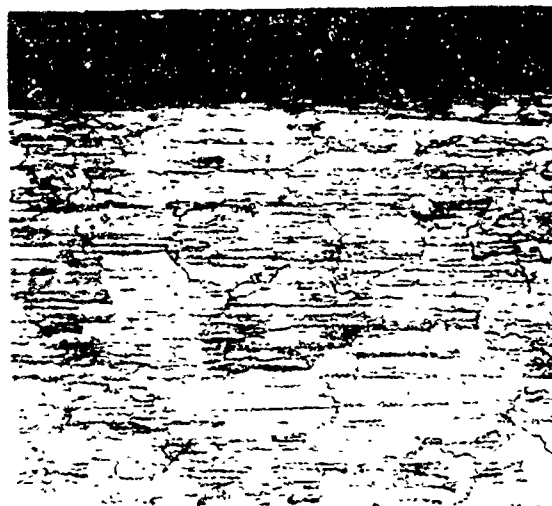
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Figure 1 . Photomicrograph of Uncoated D43

250x   250x

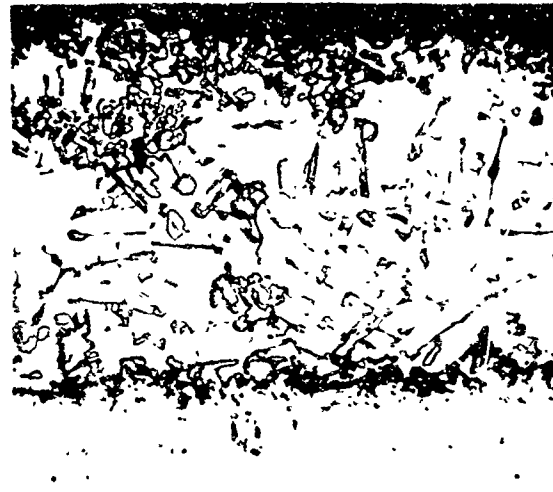TRW Cr-Ti-Si   Pfaudler PFR-32

250x

Chromizing Durak KA

Figure 2 . Typical Photomicrographs of Coated D43
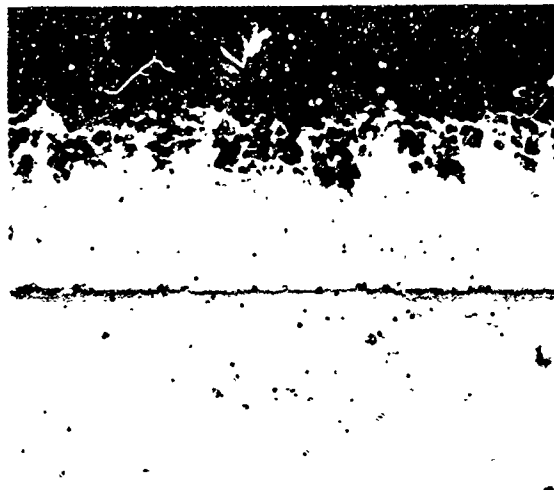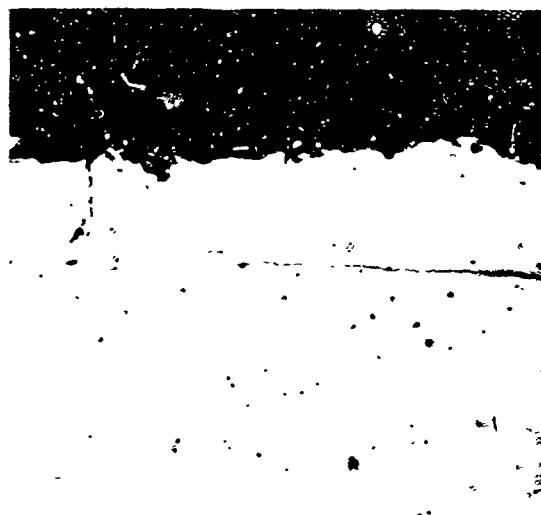
250x

LTV Modified Two-Cycle Silicide

250x

GT&E Ag-Si-Al

250x

Boeing Disil
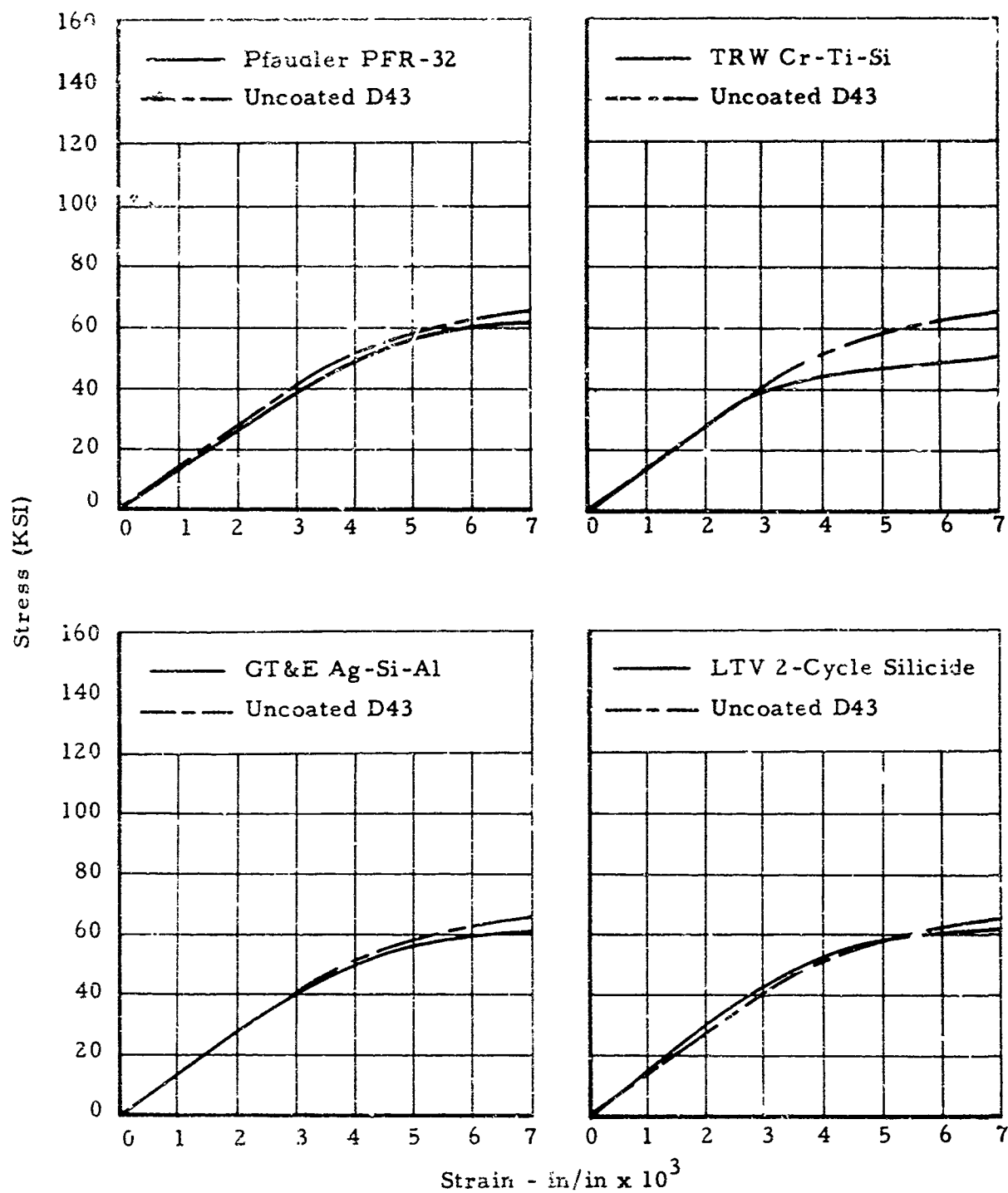
Figure 3 . Typical Photomicrographs of Coated D43

Figure 4. Typical Stress-Strain Diagrams for Coated
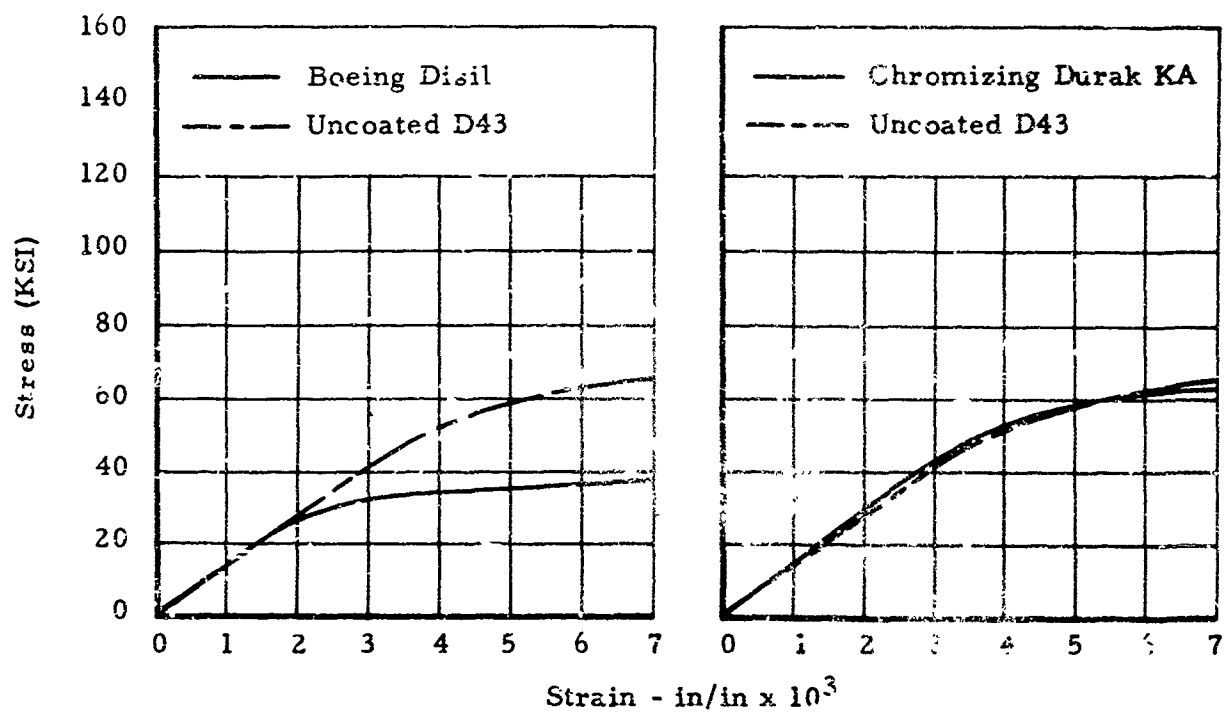D43 (Tested at Room Temperature)

Figure 5. Typical Stress-Strain Diagrams for Coated
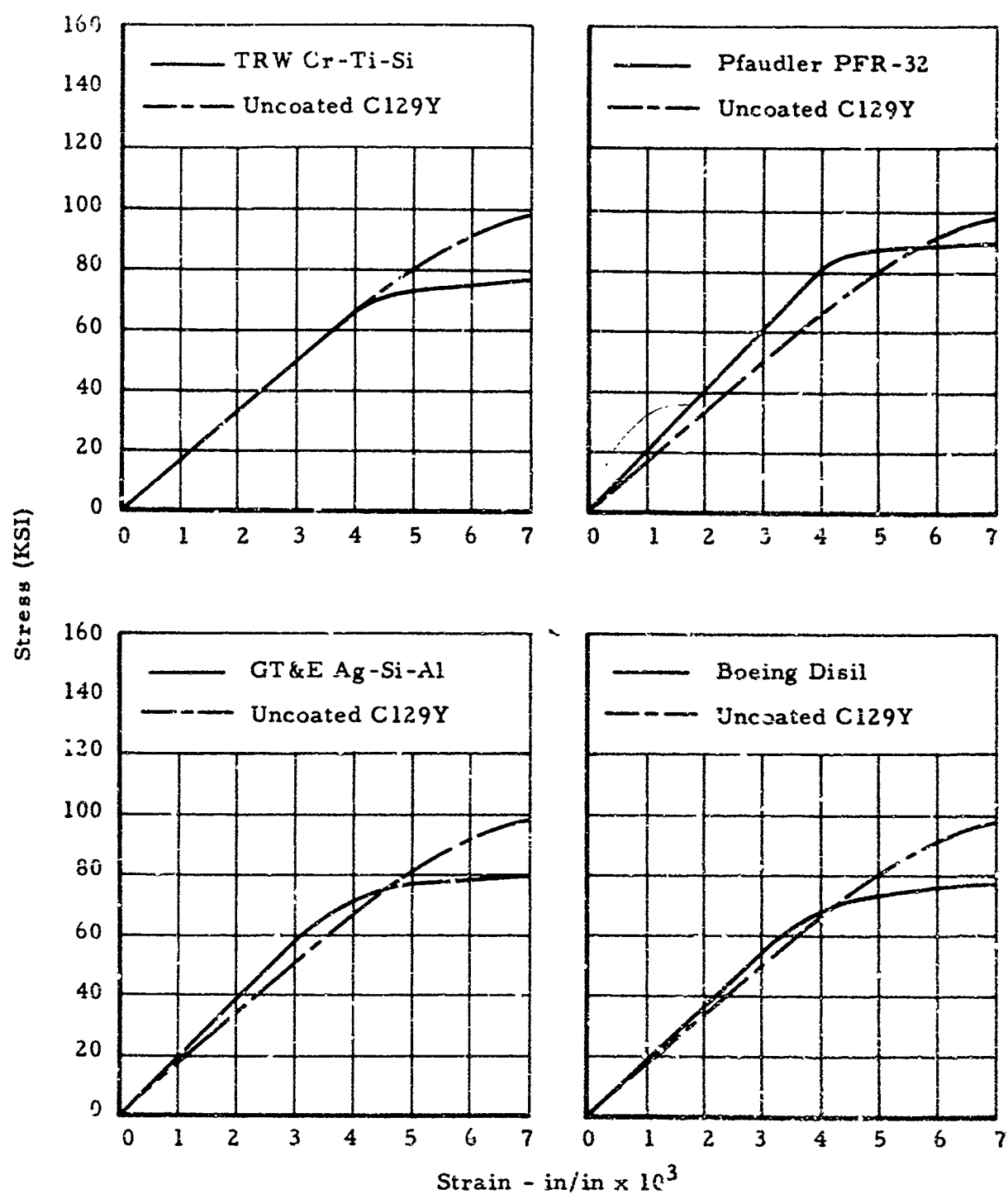D43 (Tested at Room Temperature)

Figure 6 . Typical Stress-Strain Diagrams for Coated
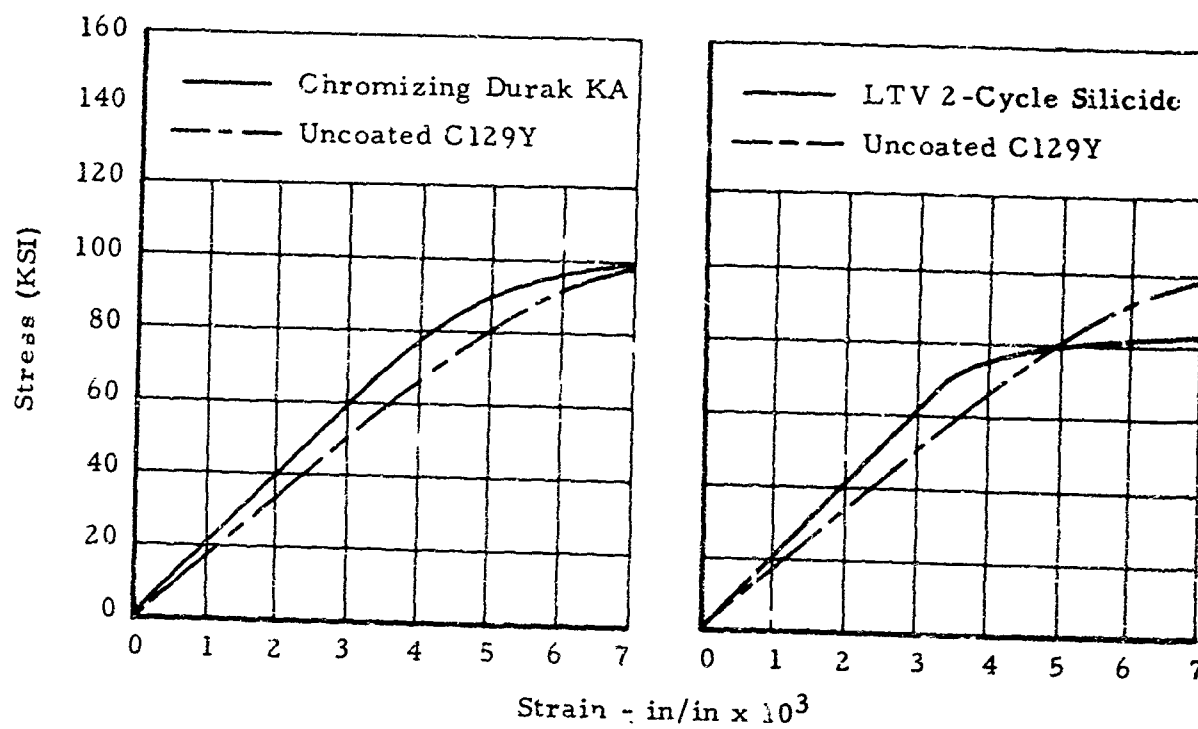C129Y (Tested at Room Temperature)

Figure 7. Typical Stress-Strain Diagrams for Coated
C129Y (Tested at Room Temperature)

Figure 9   Weibull Plot of 2600°F Cyclic Oxidation Test Results:
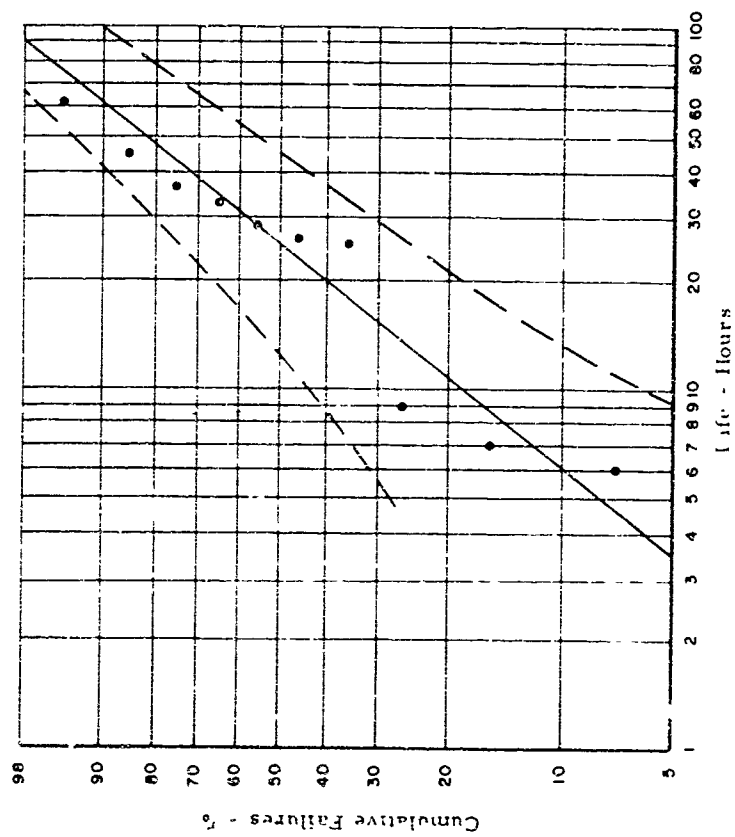   Plaudler PFR-32 Coating on 20 Mil D43

Figure 8   Weibull Plot of 2600°F Cyclic Oxidation Test Results:
            TRW Cr-Ti-Si Coating on 20 Mil D43

Figure 11. Weibull Plot of 2600°F Cyclic Oxidation Test Results;
GT&E Ag-Si-Al Coating on 20 Mil D43

Figure 10. Weibull Plot of 2600°F Cyclic Oxidation Test Results;
LTV Two-Cycle Modified Silicide Coating on 20 Mil D43

Figure 13. Weibull Plot of 2600°F Cyclic Oxidation Test Results;
Chromizing Durak KA Coating on 20 Mil C129Y
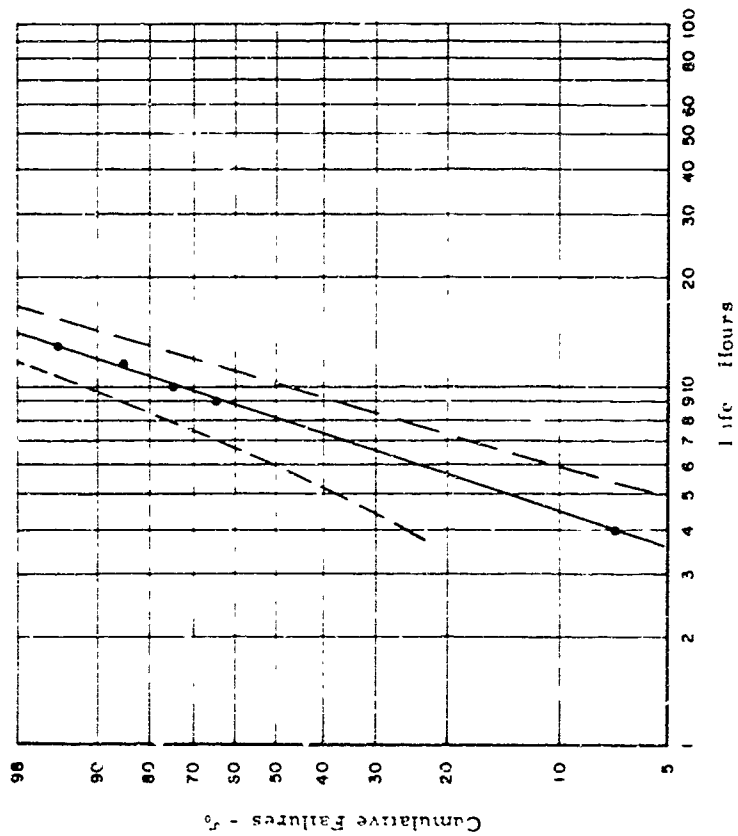
Figure 12. Weibull Plot of 2600°F Cyclic Oxidation Test Results;
Boeing Disil Coating on 20 Mil D43

Figure 15. Weibull Plot of 2600°F Cyclic Oxidation Test Results; LTV Two-Cycle Modified Silicide Coating on 20 Mil C129"
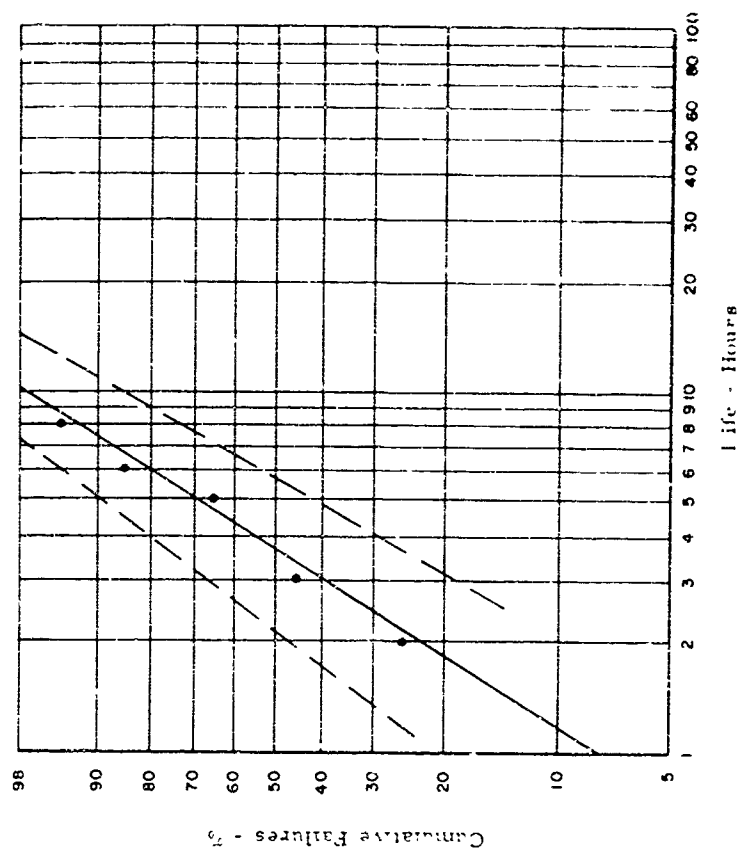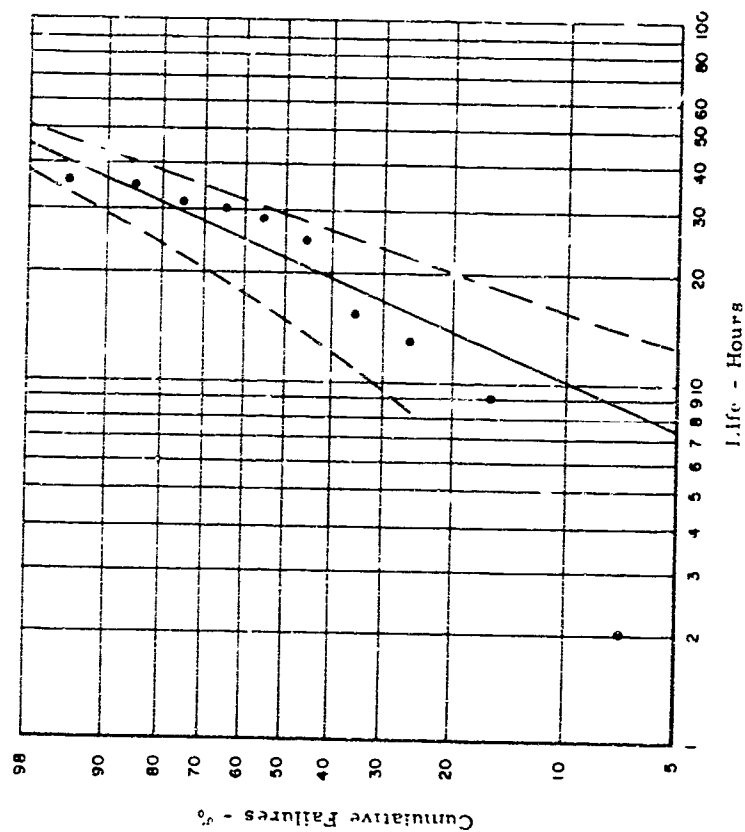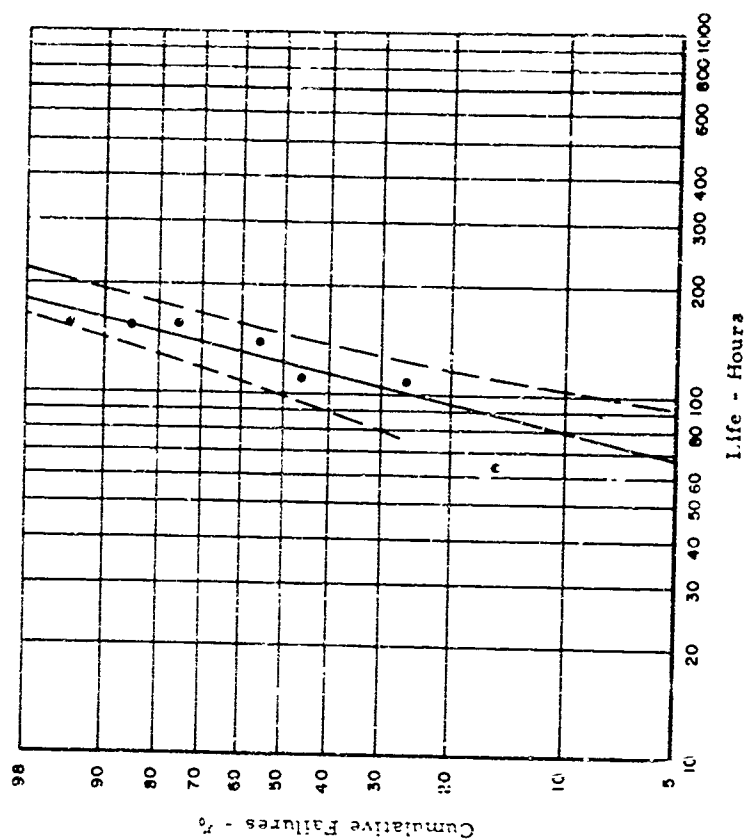
Figure 14 Weibull Plot of 2600°F Cyclic Oxidation Test Results; IRW Cr-Ti-Si Coating on 20 Mil C129Y

Figure 17. Weibull Plot of 2600°F Cyclic Oxidation Test Results; Boeing Disil Coating on) Mil C129Y

Figure 16. Weibull Plot of 2600°F Cyclic Oxidation Test Results; GT&E Ag-Si.-Al Coating on 20 Mil C129Y

Figure 19. Temperature-Time History of Phenolic Resin Impregnated Foamed Zirconia Exposed to a Heat Flux Level of 275 Btu/ft² sec

Figure 18. Temperature-Time Histories of Foamed Zirconia Exposed to a Heat Flux Level of 275 Btu/ft² sec
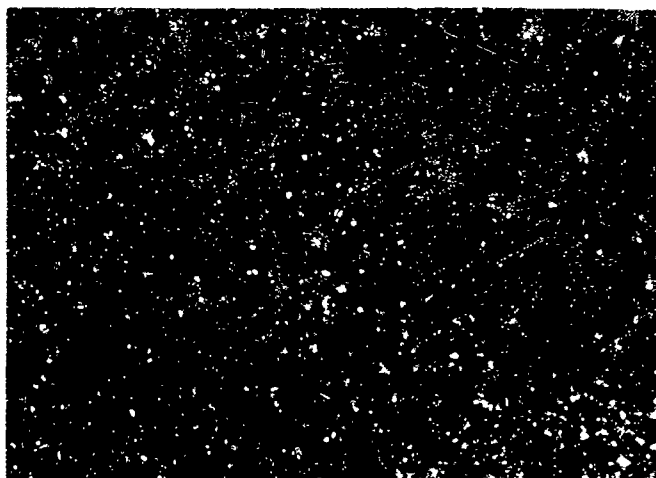
90x

Figure 20. Boride Z after 20 Minutes Exposure at
3000°F in Air at 10 mm Absolute Pressure

Table 1. Metallographic Data for Coated D4?

Coating	DPH HARDNESS				Nominal Coating Thickness (mils)	Substrate Thickness (mils)	
	Coating	Outer Intermediate Zone	Center Zone	Inner Zone	Substrate		Before	After
TRW (Cr-Ti-Si)	2930/1097*	572/946**	--	237	193	2.0	19.8	18.15
Chromizing (Durak KA)	1855/2900*	--	--	--	227	1.2	20.1	18.65
Pfaudler (PFR-32)	1534/1855*	--	--	--	254	1.8	19.7	18.4
GT&E (Ag-Si-Al)	57/2290**	1033	--	1033	262	7.2-13.6	19.7	18.0
LTV (Cr-B Modified Two-Cycle Silicide)	2900	2900	2290	1855	254	3.6	19.8	16.0
Boeing (Disil)	1855	--	--	--	265	2.4	19.3	17.2
Uncoated	--	--	--	--	265	--	--	--

*Inner Boundary/Outer Boundary

**Zone/"Islands" within Zone

Table 2. Bend Transition Temperature Measurements of Coated D43

Coating Vendor	Coating Designation	Bend Transition Temperature (t) - °F
TRW	Cr-Ti-Si	-50 > t
Chromizing	Durak KA	-50 > t
Pfaudler	PFR-32	75 < t < 125
GT&E	R508	-50 > t
LTV	Cr-B Modified Two-Cycle Silicide	0 < t < 25
Boeing	Disil	-50 > t

Table 3. Bend Transition Temperature Measurements of Coated C129Y

Coating Vendor	Coating Designation	Bend Transition Temperature (t) - °F
TRW	Cr-Ti-Si	-50 > t
Chromizing	Durak KA	-50 > t
Pfaudler	PFR-32	125 < t < 150
GT&E	R508	-50 > t
LTV	Cr-B Modified Two-Cycle Silicide	0 < t < 25
Boeing	Disil	-50 > t

Table 4   Room Temperature Tensile Test Results
for Coated D43 Columbium Alloy

| Coating | Tensile Strength ksi | | Ultimate Elongation % |
	Yield*	Ultimate	
TRW - Cr-Ti-Si	45. 0 (. 77)	62. 5 (. 75)	10. 5 (. 55)
	44. 0 (. 75)	58. 0 (. 70)	7. 6 (. 40)
Pfaudler - PFR-32	59. 0 (. 99)	85. 5 (1. 03)	10. 7 (. 56)
	60. 0 (1. 02)	86. 5 (1. 04)	13. 1 (. 69)
	55. 0 (. 94)	84. 0 (1. 01)	13. 2 (. 70)
Chromizing - Durak KA	57. 5 (. 98)	81. 5 (. 98)	12. 7 (. 67)
	58. 5 (1. 0)	82. 5 (. 99)	12. 7 (. 67)
	57. 5 (. 98)	79. 0 (. 95)	12. 7 (. 67)
LTV - Cr-B Modified Silicide	60. 0 (1. 02)	85. 5 (1. 02)	11. 4 (. 60)
	66. 3 (1. 13)	84. 0 (1. 01)	10. 4 (. 55)
	66. 0 (1. 13)	80. 0 (. 96)	10. 3 (. 54)
GT&E - Ag-Si-Al	54. 0 (. 92)	77. 0 (. 93)	10. 7 (. 56)**
	55. 5 (. 95)	78. 0 (. 94)	10. 7 (. 56)
	50. 0 (. 85)	78. 5 (. 94)	14. 0 (. 74)
Boeing - Disil	35. 0 (. 60)	49. 4 (. 59)	14. 8 (. 78)
Uncoated	57. 5	83. 3	20. 3
	56. 8	83. 2	18. 3
	61. 2	83. 2	18. 6

*0. 1% offset

**Broke outside gage length

NOTE: All stress values were based upon original substrate dimensions.
Tests were conducted at a strain rate of 0. 05 in/in/min. The
numbers in parentheses represent the ratio of coated to average
uncoated values.

Table 5. Room Temperature Tensile Test Results for Coated C129Y Columbium Alloy

Coating	Tensile Strength ksi		Ultimate Elongation %
	Yield*	Ultimate	
TRW - Cr-Ti-Si	76.0 (.78)	90.0 (.80)	20.9 (1.60)
	75.0 (.77)	87.6 (.78)	20.3 (1.55)
	72.0 (.75)	83.0 (.73)	20.9 (1.60)
Pfaudler - PFR-32	91.0 (.94)	111.0 (.98)	13.5 (1.03)
	87.0 (.90)	95.6 (.85)	8.5 (.65)**
	88.0 (.91)	99.0 (.88)	11.0 (.84)
Chromizing - Durak KA	96.0 (.99)	106.0 (.94)	15.4 (1.18)
	103.0 (1.06)	110.0 (.97)	12.8 (.98)
	97.0 (1.00)	103.2 (.91)	14.8 (1.13)
LTV - Cr-B Modified Silicide	78.0 (.80)	90.8 (.80)	13.8 (1.05)
	80.5 (.83)	85.7 (.76)	15.3 (1.17)
	--	90.8 (.80)	14.9 (1.14)
GT&E - Ag-Si-Al	78.0 (.80)	87.2 (.77)	16.2 (1.24)
	79.0 (.81)	90.6 (.80)	16.2 (1.24)
	73.0 (.75)	86.0 (.76)	15.5 (1.18)
Boeing - Disil	77.5 (.80)	88.0 (.78)	19.0 (1.45)
	71.5 (.74)	87.0 (.77)	18.9 (1.44)
	74.0 (.76)	85.2 (.75)	18.9 (1.44)
Uncoated	92.5	109.0	11.8
	100.0	114.0	13.8
	98.6	116.2	13.8

*0.1% offset

**Broke outside gage length

NOTE: All stress values were based upon original substrate dimensions.
Tests were conducted at a strain rate of 0.05 in/in/min. The
numbers in parentheses represent the ratio of coated to average
uncoated values.

Table 6 . Cyclic Oxidation Test at 2600°F
of Coated D43 Columbium

Coating	Designation	One Hour Cycles to Failure
TRW	Cr-Ti-Si	6(e), 7(e), 9(e), 25(e), 26(e), 29(e), 33(s), 36(e), 44(s), 61(e)
Chromizing	Durak KA	2(s), 2(s), 5(s), 6(e-s), 6(e-s), 6(e), 6(e-s), 6(e-s)
Pfaudler	PFR-32	2(e), 2(e), 2(e), 3(e-s), 3(s), 5(s), 5(s), 6(s), 6(s), 8(s)
GT&E	R508	63(e), 63(c), 110(e), 112(s), 117(c), 138(s), 144(e-s), 153(c), 153(c), 155(c)
LTV	Cr-B Modified Silicide	2(e), 9(e), 13(s), 15(e), 24(c), 28(e), 30(e), 31(e), 34(e), 35(e)
Boeing	Disil	4(s), 9(s), 9(s), 9(s), 9(s), 9(s), 9(s), 10(c), 12(s), 13(e)

NOTE: Letters in parentheses refer to failure location; i.e., e = edge, s = surface, c = catastrophic.

Table 7. Cyclic Oxidation Test at 2600°F
of Coated C129Y Columbium.

Coating	Designation	One Hour Cycles to Failure
TRW	Cr-Ti-Si	25(e), 37(s), 37(s), 37(s), 37(s), 37(s), 55(s), 69(s-e), 89(s), 92(s)
Chromizing	Durak KA	3(s), 8(s-e), 8(s), 8(e), 8(e), 8(s), 8(s), 9(s), 9(s), 11(s)
Pfaudler	PFR-32	6(s) - All ten specimens
GT&E	R508	68(e), 106(e), 108(c), 112(e), 115(c), 116(c), 120(s), 127(e), 128(e), 129(s)
LTV	Cr-B Modified Silicide	2(c), 2(c), 2(c), 2(e), 2(c), 2(e-s), 3(e), 4(c), 6(s), 15(e)
Boeing	Disil	2(e), 2(e), 2(e), 4(e), 4(e), 17(e), 18(e), 23(e), 25(e), 27(e)

NOTE· Letters in parentheses refer to failure location; i.e., e = edge, s = surface, c = catastrophic.

Table 8. Probable Cyclic Oxidation Life at 2600°F of
Coated D43 for Various Levels of Reliability

Coating	Coating Life (Hours) at Specified Levels of Reliability		
	70%	90%	95%
TRW - Cr-Ti-Si	16	6	3-4
Pfaudler - PFR-32	2-3	1	<1
Chromizing - Durak KA	2-3	1-2	1-2
LTV - Cr-B Modified Two-Cycle Silicide	17	10	7-8
GT&E - Ag-Si-Al	110	80	68
Boeing - Disil	6-7	4-5	3-4

Table 9. Probable Cyclic Oxidation Life at 2600°F of
Coated C129Y for Various Levels of Reliability

Coating	Coating Life (Hours) at Specified Levels of Reliability		
	70%	90%	95%
TRW - Cr-Ti-Si	40	25	20
Pfaudler - PFR-32	(All specimens tested failed after 6 hours)		
Chromizing - Durak KA	4	2	1-2
LTV - Cr-B Modified Two-Cycle Silicide	<1	<1	<1
GT&E - Ag-Si-Al	115-120	110	95
Boeing - Disil	2	<1	<1

Table 10. Test Conditions and Results for Manufacturer I Foamed ZrO_2 Specimens

		Low Density Foam		Medium Density Foam		High Density Foam	
Test Conditions	Heat Flux (BTU/ft²-sec)	275		275		275	
	Gas Enthalpy (BTU/lb)	2580	2630	2590	2580	2580	2590
	Test Duration (sec)	300		300		300	
	Stagnation Pressure (psig)	0.577	0.570	0.570	0.577	0.577	0.570
	Gas Temperature (°F)	5910	5960	5920	5910	5910	5920
	Gas Velocity (ft/sec)	890	890	880	890	890	860
Test Results	Decrease in Weight — Gms	0.52	0.55	0.47	0.43	0.47	0.29
	Decrease in Weight — %	1.9	2.0	1.6	1.6	1.2	0.7
	Density (gm/cc) — Before	0.99	0.99	1.06	1.06	1.24	1.24
	Density (gm/cc) — After	0.99	0.99	1.06	1.06	1.24	1.24
	Depth of Erosion (in.)	-0.005	-0.003	-0.005	-0.012	-0.008	-0.012
	Volume of Erosion (in³)	--	--	--	--	--	--
	Final Back Face Temp °F	2260	2310	1640	2360	1450	1000
	Final Front Face Temp °F	4245	4225	4250	4190	4155	4120
	Remarks	Both specimens cracked during test.		One specimen (shown below) cracked during test; the other remained intact.		One specimen (shown below) cracked during test; the other remained intact.	
	Sample Appearance						

Table 11. Test Conditions and Results for Manufacturer I Foamed ZrO_2 Specimens Impregnated with Phenolic Resin
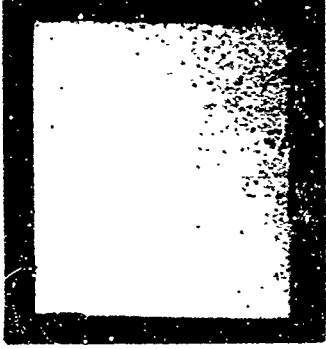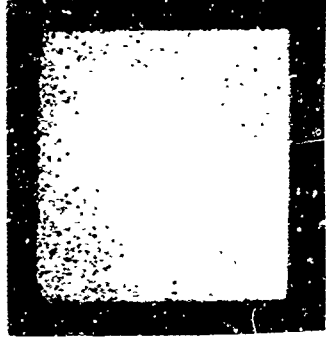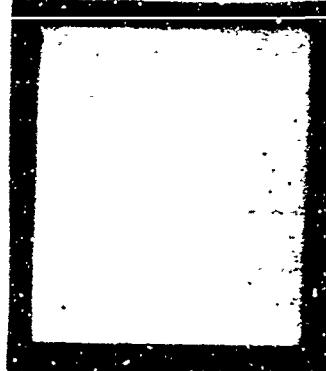
Material		Low Density Foam		Medium Density Foam		High Density Foam	
Test Conditions	Heat Flux (BTU/ft²-sec)	275		275		275	
	Gas Enthalpy (BTU/lb)	2580*	2630**	2580*	2580**	2580	2560
	Test Duration (sec)	300		300		300	
	Stagnation Pressure (psig)	0.577	0.570	0.570	0.577	0.577	0.570
	Gas Temperature (°F)	5910	5960	5920	5910	5910	5890
	Gas Velocity (ft/sec)	890	880	880	890	890	880
Test Results	Decrease in Weight — Gms	16.54	17.04	15.82	16.35	17.16	17.97
	Decrease in Weight — %	34.2	35.1	32.1	33.3	27.5	28.4
	Density (gm/cc) Before	1.89	1.86	1.93	1.93	2.11	2.07
	Density (gm/cc) After	--	--	--	--	--	--
	Depth of Erosion (in.)	-0.018	-0.019	-0.013	-0.016	-0.020	-0.025
	Volume of Erosion (in³)	0.825	0.832	0.754	0.773	0.846	0.826
	Final Back Face Temp °F	1660	1650	1545	1585	1380	1460
	Final Front Face Temp °F	4190	4245	4180	4100	3940	4100
	Remarks	*42.8 w/o Phenolic Resin	**43.3 w/o Phenolic Resin	*40.8 w/o Phenolic Resin	**41.3 w/o Phenolic Resin	*34.8 w/o Phenolic Resin	**33.0 w/o Phenolic Resin
	Sample Appearance						

Table 12. Results of Coating Bond Strength Tests

System	Spray Settings Dist. (in.)	Power (KW)	Total Thickness (in.)	Bond Strength (psi)	Comments
NiAl	3	18	.018	290	The average bond
Al_2O_3	3	28		260	strength, 485 psi.
				480	Break occurred
				395	in NiAl flashing.
				1000	
				Ave. 485	
NiCr	4	18	.013	2090	Average bond
ZrO_2	4	30		1568	strength, 1480
				1277	psi. Break
				1240	occurred in the
				1225	ZrO_2 top coating.
				Ave. 1480	
NiAl	4	18	.014	840	Average bond
Ni Coated Al_2O_3	3	26		840	strength, 860
Al_2O_3	4	26		860	psi. Break
				870	occurred in the
				900	Al_2O_3 top coating
				Ave. 860	and Ni coated
					Al_2O_3 interface.
NiAl	4	18	.016	1560	Average bond
Graded NiAl-Al_2O_3	5	28		1840	strength, 1760
Al_2O_3	5	28		1890	psi. Break
				1682	occurred in
				Ave. 1760	Al_2O_3 topcoat.
Mo	3	18	.011	2950	Average bond
Graded NiCr-ZrO_2	5	28		2150	strength, 2690
ZrO_2	5	28		3360	psi. Break
				2390	occurred in NiCr-
				2575	ZrO_2 and ZrO_2
				Ave. 2690	interface and in
					ZrO_2 topcoating.

Table 13. Results of Low Pressure Oxidation Tests
of Several Ceramic Composites

Material	Test Condition*	Wt. Change %	Observations
Boride Z			
1	0.5 mm Hg Pressure	-.3	Average weight loss 0.8%.
2		-.4	Loss of metallic luster on
3		-.5	surface. Possible surface
4		-1.3	film formed during exposure.
5		-1.7	
6	10 mm Hg Pressure	-1.2	Average weight loss 1.2%.
7		-1.7	A dense white crystalline
8		-.9	coating formed on exposed
9		-1.1	surfaces. Cross section
10		-.11	cut showed a dark discolored
			intermediate zone between
			surface coating and metallic
			luster of core.
11	760 mm Hg Pressure	+.7	Average weight gain 0.8%.
12		+.9	Surface covered with a
13		+.9	glassy coating. Cross-
14		+.8	section shows thin, dark
15			intermediate zone.
JTA			
1	0.5 mm Hg Pressure	-5.1	Average weight loss 3.63%.
2		-4.1	White crystalline grains
3		-2.3	dispersed over surface.
4		-4.0	
5		-2.6	
6	10 mm Hg Pressure	-12.3	Average weight loss 13.2%.
7		-14.3	Very friable porous crys-
8		-11.3	talline coating easily parted
9			from surface.
10		-14.9	
11	760 mm Hg Pressure	-2.8	Average weight loss 2.9%.
12		-2.7	White glassy coating
13		-3.4	lightly adhered to surface.
14		-4.0	
15		-1.7	

Table 13 (Cont'd)

Material	Test Condition*	Wt. Change %	Observations
Modified SiC			
1	0.5 mm Hg Pressure	-15.9	Average weight loss 13.1%.
2		-8.0	Surface eroded by oxidation.
3		-15.8	Some sign of glassy phases
4		-14.6	distributed about surface.
5		-11.0	
6	10 mm Hg Pressure	+52.8	Average weight loss 30.5%.
7		-39.4	Severe surface erosion.
8		-17.1	Porous glassy coating
9		-10.8	formed on surface easily
10		-31.3	parted. Eroded areas
			covered with small glass
			fibers.
11	760 mm Hg Pressure	+0.5	Average weight gain 0.9%.
12		+0.4	Glassy surface film.
13		+0.4	
14		+0.4	
15		+0.4	
SiC			
1	0.5 mm Hg Pressure	-36.8	Average weight loss 39.6%.
2		-32.8	Brown glassy film on
3		-34.2	surface.
4	10 mm Hg Pressure	-20.5	Glass coating formed on
5			surface but easily parted.
6			Surface showed areas of
			erosion.
7	760 mm Hg Pressure	+.74	Average weight gain .61%.
8		+.56	Porous bubble glassy surface
9		+.54	coating formed.

*All exposures were at 3000°F for 20 minutes in an air environment.

END 4-66